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THE USE OF DTA IN THE ANALYSIS OF SILVER (II) OXIDE FOR CARBONATE IMPURITY

P. A. BARNES and R. M. TOMLINSON

Department of Chemistry, Leeds Polytechnic, Leeds LS1 3HE U. K.

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A rapid and reliable method is described in which quantitative differential thermal analysis is used to analyse for silver carbonate in the presence of silver(II) oxide. The method is applicable quantitatively above 20% silver carbonate and semi-quantitatively above 5%.

The solid-state chemistry of silver (II) oxide is of both commercial and academic interest. Originally thought to be peroxide, it is now known [1] to be a true oxide containing both mono and trivalent silver. While much of the published work is related to the silver oxide cell [2, 3], the structure of the solid [4] and its thermal composition [5, 6], little is known of its behaviour in gas solid reactions. As part of an investigation into the reaction with carbon dioxide a simple and rapid method of analysing for the product, silver carbonate, was required. Many of the classical techniques for the analysis of silver (II) oxide proved unsatisfactory as they give only the amount of "divalent" silver [7]. Silver (I) oxide and metallic silver are probably also present in the higher oxide and hence the silver carbonate cannot be estimated by difference.

As the work involved thermoanalytical techniques it was decided to investigate the possibility of their use in the analysis for silver carbonate. Previous workers [8] used thermogravimetry and differential scanning calorimetry in the analysis of pure silver (II) oxide prepared in the absence of carbon dioxide. They used a dry nitrogen atmosphere, presumably static, and found the decomposition to consist of a small exotherm at ca. 430 K due to the reaction

$$2AgO \rightarrow Ag_2O + \frac{1}{2} O_2 \qquad (1)$$

and an endotherm at ca. 700 K corresponding to

$$Ag_2O \rightarrow 2Ag + \frac{1}{2} O_2 . \qquad (2)$$

Silver carbonate decomposes in two stages. The first is given by equation (3), the second by equation (2)

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 . \qquad (3)$$

No work appears to have been done on the analysis of silver (II) oxide containing relatively large concentrations of silver carbonate.

A thermoanalytical study of this latter material [9] has shown it to decompose in a complex manner. Essentially, for the commonly found modification, a small irreversible exotherm at 440 K is followed by two reversible endothermic phase changes at 450 and 470 K, a carbonate decomposition endotherm at 500 K and a final endotherm, due to the decomposition of silver (I) oxide at 650 K.

Despite some overlap between the small silver (II) oxide decomposition exotherm and the large silver-carbonate endotherms, an attempt was made to analyse for the latter material in presence of a large proportion of the former.

Experimental

A Stanton Redcroft differential thermal analyser was used with flat-bottomed open aluminium pans. A dynamic atmosphere of nitrogen flowing at 20 cm^3 per minute was employed and calcined alumina was used as the reference material. Care was taken to standardise the variables associated with the sample by using a constant weight of material (10 mg ± 50 μg) and by the adoption of a standardised packing procedure. Initial exploratory DTA curves were obtained at different heating rates and the highest rate consistent with reproducible traces (15 K min^{-1}) was chosen. All other parameters amenable to control i.e., the ΔT amplification and recorder input were kept constant.

Thermogravimetry was performed with a Stanton Redcroft TG 750 thermobalance and plots of fractional percentage weight loss were recorded directly. The balance was used with a flowing atmosphere of dry nitrogen (20 cm^3 min^{-1}), a heating rate of 15 K min^{-1} and a full scale sensitivity of 2.5 mg. The sample weights were chosen to give approximately full scale deflection and ranged from 11 mg for silver carbonate to 16 mg for silver (II) oxide.

Silver (II) oxide and silver carbonate were used as obtained from B.D.H. Ltd. Analysis of the silver (II) oxide by the volumetric method recommended by Lloyd [7] gave a purity of 88.8 ± 0.4%. The total silver content was determined by Volhard's technique which gave the silver found as 87.1 ± 0.3% (theoretical value 87.1%). The latter technique also gave the purity of the silver carbonate as 100.1 ± 0.2%.

X-ray diffraction powder photographs were used to identify the products of the reactions. A Philips camera of 114.83 mm diameter and the Debye-Scherrer technique were employed.

Results

Details of the main DTA-peak temperatures and the weight-loss temperature ranges found in TG experiments for the decomposition of silver (II) oxide and silver carbonate are given in Table I. Typical curves are shown in Figs 1a and 1b, respectively.

X-ray diffraction results confirmed the following interpretation of the DTA and TG curves. The silver (II) oxide used exhibited two exotherms, the first of which was responsible for only a minor weight loss, the second resulting from the decomposition of the bulk of the silver (II) oxide to silver (I) oxide. An endotherm due to the breakdown of this latter material to metallic silver was found at 690 K. The silver carbonate showed three endotherms at low temperature, appearing here as a complex peak, during which reaction 3 occurred. The small exotherm sometimes found at 440 K [9] was absent. The final endothermic decomposition of the silver (I) oxide (reaction 2) was found at 650 K.

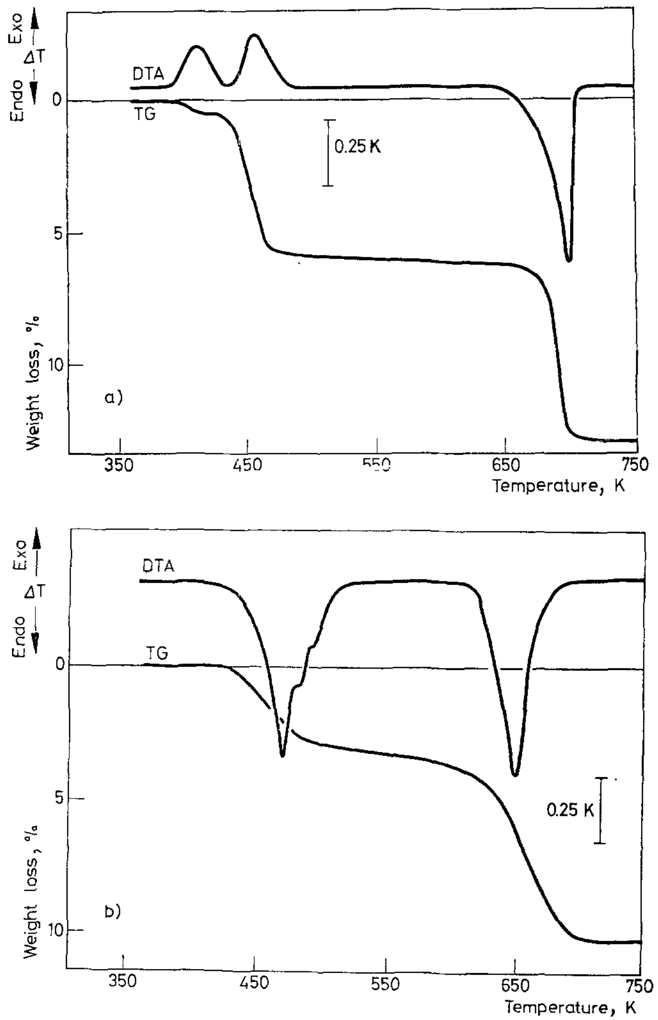

Fig. 1. DTA and TG curves for (a) silver(II) oxide and (b) silver carbonate. Heating rate, 15K min^{-1}; atmosphere, nitrogen flowing at 20 cm^3 min^{-1}. Sample weights, DTA 10 mg; TG of AgO 16 mg, TG of Ag_2CO_3 11 mg

Table 1

Peak temperatures and weight-loss-temperature ranges for the decomposition of silver(II) oxide and silver carbonate

	DTA-peak temperature/K		Weight-loss-temperature range/K	
	AgO	Ag_2CO_3	AgO	Ag_2CO_3
Initial decomposition	410 460	470 480 490	390—420 430—500	430—520
Final decomposition	690	650	640—720	550—700

Table 2

Results obtained to demonstrate the homogeneity of mixtures of silver(II) oxide and silver carbonate

% AgO used in mixture	% AgO found by analysis	% difference
71.6	71.6	0
52.5	52.6	0.19
35.8	35.8	0
17.4	17.6	1.2

It will be seen from the results (Table 1) that the initial decompositions of silver (II) oxide (equation 1) and silver carbonate (equation 3) occur in the same temperature range. It was found that the resolution of conventional TG was insufficient to distinguish between these two processes, the TG of a mixture of the two materials being a smooth curve.

The situation proved to be more favourable with DTA, as reaction 1 is exothermic while reaction 3 is endothermic. As shown by Fig. 2, this enabled the two processes to be distinguished, but it is clear that there is some overlap between the two peaks. Nevertheless, there should exist a relationship, possibly non-linear, between the silver-carbonate-content of the silver (II) oxide and the area under the complex silver-carbonate-decomposition endotherm. It should be noted that the enthalpy of reaction 1 is -2.51 kJ mol^{-1} [8], while that of reaction 3 is of opposite sign [10] and of greater magnitude. In addition, the silver carbonate undergoes two phase changes [9] both endothermic, which overlap the decomposition peak giving a composite endotherm of enhanced magnitude. Thus the silver (II) oxide-decomposition peak and the silver-carbonate endotherm are of approximately equal area at a concentration of 20% silver carbonate, a fact which contributes to the accuracy of the method at higher levels of silver (II) oxide.

In order to test the linearity of the method, mixtures of silver (II) oxide and silver carbonate were made by thoroughly mixing accurately weighed amounts of the two solids. A microbalance was used in the preparation of the calibration mixtures and weighing errors were less than 0.1 %. In any calibration process using mixtures of solids, care must be taken to ensure homogeneity of the product. This was investigated by analysing samples from each mixture for silver (II) oxide using the volumetric iodide method recommended by Lloyd [7]. The silver (II) oxide was of known purity, for which correction was made, and typical results are shown in Table 2. The discrepancies found in all cases were less than the errors inherent in the DTA method and it was concluded that the method of mixing was satisfactory for the present purpose.

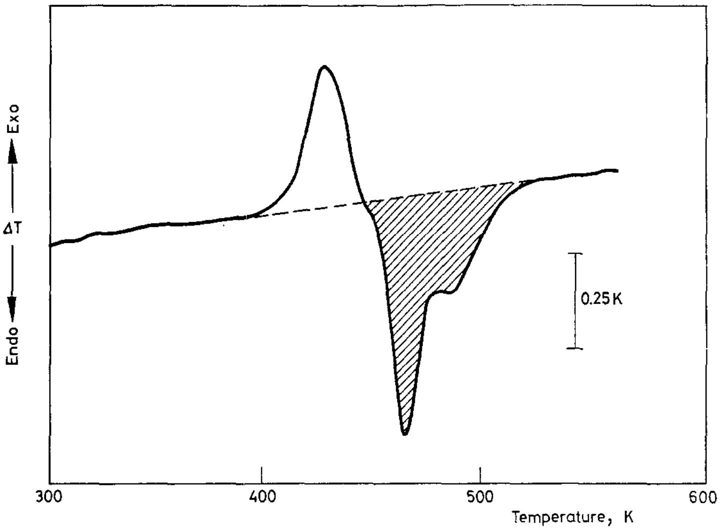

Fig. 2. DTA trace of a mixture of 40 % silver carbonate, 60 % silver(II) oxide. Heating rate 15K $\min^{-1}$; atmosphere nitrogen flowing at 20 cm^3 $\min^{-1}$, sample weight 10 mg

Differential thermal analysis was performed on the calibration mixtures under the standardized conditions mentioned above, and the area of that part of the curve due to the decomposition of silver carbonate measured (Fig. 2). The peak-area determination was performed by weighing photostat copies of the curve, using a microbalance. The peak traces obtained weighed between 20 and 200 mg and the lower weight corresponded to several square inches of chart paper. Application of the method of least squares to the resulting straight line calibration graph gave the following relationship.

$$x = 0.498y + 2.52$$

where y = peak area of the "carbonate" endotherm measured in the arbitrary units of mg of paper;
x = the percentage of silver carbonate.

Because of the arbitrary nature of the peak area measurement and the different sensitivities of various types of equipment, the values of the two constants will depend on the characteristics of individual pieces of equipment.

It was found that the mean deviation from the line was 3.0% above a level of 20% silver carbonate. Below this limit, because of the decreasing size of the silver-carbonate peak, the results were less reproducible, but semiquantitative work proved to be possible down to a value of 5% silver carbonate where the deviations of ±20% could be expected.

In order to check the validity of the calibration, a mixture containing 40.0% of Ag_2CO_3 was prepared and analysed by the above DTA method. The experimental value found was 38.0%.

Discussion

When using DTA for quantitative analysis it is usual to select a peak free from interference. It is clear that, in the method described, the silver carbonate peak is reduced by an amount proportional to the amount of silver (II) oxide present, this being illustrated by the intercept of the calibration curve. The technique is thus semi-empirical, but nevertheless it gives a linear relation over the range of compositions used.

One of the problems associated with work of this kind is the effect of the reactive self-generated atmosphere on the decomposition endotherms. That the results are of a precision usually associated with quantitative DTA indicates that the dynamic atmosphere reduced the carbon dioxide level to a value well below the equilibrium pressure. Undoubtedly, the small sample weight, the open sample pan and the small swept volume of the sample chamber were instrumental in reducing diffusion effects.

It has been reported [11] that, given good control of the variables involved in DTA, results reproducible to ±5% can be obtained routinely, and to ±1 –2%, given extreme precautions. The method described yields results falling into the former category above 20% impurity while giving an indication of the silver carbonate level down to 5%.

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